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FIRST ANNUAL REPORT
"PLASMA JET CHEMISTRY"

BY

A. V. GROSSE, H. W. LEUTNER AND C. S. STOKES

DECEMBER 31, 1961

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FIRST ANNUAL REPORT
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INTRODUCTION

The plasma jet is a relatively new device for the production of high temperatures beyond the range of chemical-combustion flames or the ordinary electric arc. Its range may be defined as about 5000°K. - 50,000°K.

Very few studies have been carried out on the use of the plasma jet for chemical synthesis. A review of all plasma jet synthesis research up to 1959 was presented by R. C. Phillips and F. A. Ferguson.[1] The Research Institute of Temple University has contributed during the past two years several papers dealing with the investigation of plasma-jet properties and chemical synthesis in a plasma jet.[2-4]

(1) R. C. Phillips and F. A. Ferguson, "High Temperature Chemical Synthesis," Symposium on High Temperature Technology, Asilomar Chemical Grounds, California, Oct. 6-9, 1959, pp. 315-322.

(2) C. S. Stokes, W. W. Knipe and L. A. Streng, "Heat Transfer Rate of an Argon Plasma Jet," J. Electrochem. Soc., 107, 35 (1960).

(3) C. S. Stokes and W. W. Knipe, "The Use of the Plasma Jet in Chemical Synthesis," Ind. & Eng. Chem., 52, 287 (1960).

(4) H. W. Leutner and C. S. Stokes, "Production of Acetylene from the Elements and from Methane Using a Plasma Jet," Ind. & Eng. Chem., 53, 341 (1961).

SUMMARY

Two types of plasma jets were built and used: a D.C. high intensity plasma jet and a radiofrequency plasma jet. A detailed description of the devices, their operating conditions and characteristics are presented.

Detailed descriptions are given of the preparation of several gaseous endothermic compounds with the plasma jet, such as cyanogen, $(CN)_2$, hydrocyanic acid, HCN, acetylene, C_2H_2, and the oxides of nitrogen. Various methods of preparation of the compounds cited above are reported.

The use of the plasma jet as a reducing device for oxides was tested with aluminum oxide. Although the investigations are not completed, the results of the first experiments are included.

I. PLASMA JET EQUIPMENT

A. High Intensity D.C. Plasma Jet

1. The Plasma Jet

Two essentially different plasma generators were used. Both were redesigns of the earlier forms.[2-4] They allow operation with noble gases, such as helium and argon, and with nitrogen and mixtures of argon and hydrogen. Fisher and Porter flow meters controlled the gas flows. An Airco Bumblebee 750 amp d.c. welder served as the power source. Appropriate electrical meters shown in Fig. 1 guided the operation. Starting the arc was accomplished by "shorting out" the electrodes.

a. Plasma jet with a nonconsumable cathode:-- Figures 2, 3 and 4 are sketches of the apparatus used. A 1/8"-diameter 2% thoriated tungsten rod was used as the nonconsumable cathode. It was strongly water-cooled (water pressure 75 lbs/in.^{2}). The gas was fed through an annulus around the cathode with six equally spaced holes.

The anode consisted of a water-cooled removable copper insert pressed into a stainless-steel holder using O-ring seals. When using nitrogen as plasma gas, it was necessary to use a 1/16" thick graphite insert (7/16" in diameter) in the copper anode to protect the anode from melting. When using the noble gases, this precaution was not necessary. The electrodes were separated by a nylon case which served as insulator and contained the cathode assembly.

b. Plasma jet with a consumable cathode:-- Figure 5 shows the electrode design for a plasma jet using consumable graphite electrodes. The cathode consisted of a water-cooled copper liner in which 1/4"-diameter rods of either ordinary or pyrolitic graphite were placed. These rods were pushed mechanically towards the anode, according to the vaporization rate of the graphite. The anode and the gas-feeding system were the same as those described under a. A 5/8"-diameter anode was used for thicker graphite cathodes.

2. Gas and Powder Feeding Devices

Three different types of devices were used to feed gases and powdered materials into the plasma "flame." The devices could be attached directly to the plasma generator.

a. Single orifice feeder for powdered materials:-- A water-cooled brass ring with a 1/8"-diameter brass tube was used. The tube was located 1/2" below the anode of the jet. The solid particles were fed by using either an inert or a reactive carrier gas, see Fig. 6.

b. Circular feeder - perpendicular to the flame axis:-- The construction of this device is similar to that described under a, see Fig. 7. Instead of a single hole, eight equally distributed 1/32" holes in a removable graphite or stainless-steel insert allowed an even gas distribution to the plasma "flame."

c. Circular feeder at a 30° angle to the flame axis:--
A thin stainless-steel ring with 16-1/32" holes drilled at an
angle of 30° was used. With this device the gases reached the
plasma flame approximately 3/4" below the anode. A detailed
drawing is given in Fig. 8.

3. Powder Feeding Apparatus

By using the fluidization principle, powdered material
(200 mesh) was constantly fed with the apparatus shown in Fig. 9.
Noble gases and hydrogen were used as carrier gases. Constant
feeding rates of 1.5 grams per minute and higher were possible.

4. Quenching Devices

A 2'-length and 2-1/2"-diameter water-cooled brass tubing
with four observation windows was attached to the feeding ring.
Through the brass bottom plate a water-cooled brass funnel (1-1/2"
o.d. x 1/2" i.d. x 6" long) could be introduced at a distance of
1" from the feeding ring, allowing a rapid quenching of the
products. In order to collect the solid product leaving the
cooling funnel, a brass collector was attached beneath the funnel.
Figure 10 is a sketch of the plasma jet with the feeding and
quenching devices used.

B. The Radiofrequency Plasma Jet

Two radiofrequency plasma jet units were built under this contract. A 0.3 KW unit for low pressure operation and a 1.5 KW unit for atmospheric pressure operation, both using oxygen, nitrogen and hydrogen.

1. The 0.3-KW Unit

This unit is a 27.5 mc power oscillator of approximately 350 watts (power input to plate), using a special water-cooled coil for the output resonance tank. The output power can be varied by either grid detuning or plate voltage.

The high-voltage end of the resonance-tank coil is attached to a 1/2"-diameter by 7" length water-cooled tube with a conical molybdenum tip, which runs through the center of the coil, see Figs. 11 and 12.

A water-cooled glass tube surrounds the top half section of the tank-coil tube. The plasma gas enters through a glass side tube at approximately 1" below the tip of the tank-coil tube.

The R.F. jet can be started easily by the use of helium.

2. The 1.5-KW Unit

A schematic drawing of the unit is shown in Figs. 13 and 14. This unit represents basically a 1.5-KW transmitter that operates between 24-28 mc. The output-tank coil is suspended

vertically on the side of the generator cabinet. The center tank coil electrode is adjustable for various load impedances. Both the center electrode and the tank coil are water-cooled. The plasma gas is injected into the top of a vycor tube which extends down through the center of the tank coil.

II. EXPERIMENTAL INVESTIGATIONS

A. The High Intensity D.C. Plasma Jet

1. Establishment of Operation Conditions

In order to obtain the optimum ranges of operation and the characteristics of the plasma jet for different gases, a series of test runs were carried out at varying gas flows and power inputs. Consumable and nonconsumable cathodes were used in all of the following experiments. Ordinary graphite inserts with a 1/16"-wall were used in the copper anode. Inserts of other materials than ordinary graphite proved to be less resistant.

a. Using nonconsumable cathodes:-- By using 1/8"-diameter 2% thoriated tungsten rods as cathodes and argon as plasma gas, stable plasma "flames" were obtained at gas flows ranging from 10 to 20 1/min. and power inputs of 8-16 KW. The results are tabulated in Table I.

To maintain a stable pure nitrogen plasma jet, a power input of at least 12.5 KW was necessary, using relatively low gas flows. The maximum power available was 16 KW; therefore, the

TABLE I

Characteristics of the Plasma Jet Using a 2% Thoriated Tungsten Cathode

Plasma Gas	Gas Flow 1/min.	Electrical Characteristics		
		Amp.	V.	KW
Argon	11.9	470	21	9.9
"	14.35	420	21	8.8
"	15.75	450	19	8.55
"	16.7	450	19	8.56
"	11.9	470	21	9.9
"	11.9	570	23	13.1
"	11.9	600	26	15.6
Nitrogen	3.85	250	50	12.5
"	3.75	270	50	12.7
"	4.15	300	45	13.5
"	5.0	300	44	13.2
"	5.0	410	36	14.75
"	7.0	420	37	15.55

operation with nitrogen as plasma gas was limited by the energy
supply of the equipment available. By using lower gas flows,
operation at lower power inputs would be possible in principle,
but in this case the cathode cooling becomes much less effective,
and the cathode melts. In these circumstances operation with
nitrogen was restricted to gas flows of 3.5 to 7.0 1/min., with
power inputs from 12.5 to 16 KW. Operation with pure nitrogen was
possible for 15 min., although more stable plasma jets, desirable
for chemical reactions, were obtained by using a gas mixture of 25%
argon and 75% nitrogen. Table I shows the characteristics of the
jet obtained in several runs. The characteristics given for the
nitrogen plasma show the nitrogen gas flow only.

b. Using consumable cathodes:-- As cathode material
ordinary ("National" special graphite electrodes from the National
Carbon Co.) and pyrolitic graphite (gift from G.E. Co. Philadelphia)
were used in the form of rods (1/4"-diameter). Ordinary graphite
is used here to mean the natural or commercial graphite with random
distribution of the graphite crystals. Thermal and electrical
properties are the same in all directions (isotropic graphite).
Pyrolitic graphite may be considered to be composed of large single
crystals of graphite which are arranged in planes forming structures
similar to benzene rings.

The electrical conductivity within the plane direction (crystallographic a-direction) is much higher than in the direction from plane to plane. (crystallographic c-direction. Anisotropic graphite). By measuring the resistivity by commonly known methods, the electrical conductivity of the pyrolitic graphite available was found to be 115 times larger in the a-direction than in the c-direction.

Ordinary graphite was vaporized very fast when using as plasma gas pure argon, pure nitrogen, argon with nitrogen and argon with hydrogen. With argon, the carbon consumption was low; it increased substantially when nitrogen and mixtures of argon with hydrogen were used. The vaporization rates ranged from .05 to 2.0 grams of carbon/min. (under extreme conditions up to 3.0 grams/min.) As was to be expected, the graphite consumption increased with the total power input and decreased with increasing gas flow. Table II gives detailed data on the operating conditions and the results of a series of experiments.

By using pyrolitic graphite as cathode, a stable plasma jet could be maintained with almost no cathode consumption, even with argon-hydrogen mixtures as plasma gases. The crystallographic a-direction (high conductivity direction) was parallel to the axis of the rod and the c-direction perpendicular to the axis. Detailed information is listed in Table II.

TABLE II

Gas	Flow Rates l/min.	Electrical Characteristics			Carbon Consumption mg./min.
		Amp.	V.	KW	
a) Using Ordinary Graphite:					
Ar	8.9	470	18.0	8.5	342.0
Ar	11.9	455	17.5	8.0	360.4
Ar	17.9	445	19.5	8.7	292.4
Ar	23.9	435	19.5	8.5	154.0
Ar	27.4	435	19.5	8.5	104.4
Ar	17.9	400	17.5	7.0	43.6
Ar	17.9	445	19.5	8.7	292.4
Ar	17.9	470	21.0	9.9	388.6
Ar	17.9	490	24.5	12.0	869.4
N_2	3.15	280	41.0	11.5	938.4
N_2	5.1	300	41.5	12.4	728.8
N_2	7.0	310	42.0	13.0	695.2
N_2	8.55	300	41.0	12.3	568.4
N_2	10.8	290	41.0	11.9	404.0
N_2	14.15	280	43.0	12.0	288.4
N_2	8.55	220	40.5	8.9	395.2
N_2	8.55	300	41.0	12.3	568.4
N_2	7.00	305	43.5	13.2	974.0
Ar H_2	20.3 6.5 (3:1)	325	28.0	9.15	954.0
Ar H_2	20.3 6.5 (3:1)	325	27.25	8.9	650.0
b) Using Pyrolitic Graphite:					
Ar N_2	23.9 5.0 (5:1)	120	45.0	5.40	3.0
Ar N_2	23.9 5.0 (5:1)	310	37.0	11.47	27.0
Ar H_2	23.9 4.0 (6:1)	150	50	7.5	11.0
Ar H_2	23.9 4.0 (6:1)	155	50	7.55	10.0

Summarizing, the results of the experiments show that ordinary graphite cannot be used as a consumable cathode to supply the carbon for compounds to be prepared in the plasma jet, such as carbides, hydrogen cyanide, cyanogen and eventually organic compounds. In contrast to ordinary graphite, pyrolitic graphite is practically nonconsumable, since the heat is easily conducted away in the longitudinal direction of the rod (a- or high conductivity direction). Pyrolitic graphite electrodes might be used for reactions where small contaminations of the metal cathode material are undesired, since small amounts of carbon contaminations will react with the usual plasma gases to form gaseous compounds: CO, CO_2, $(CN)_2$, C_2H_2, etc.

c. Other gases tested as plasma carriers:-- Besides the noble gases and nitrogen, other gases such as hydrogen, methane, carbon monoxide and ammonia, were tested as plasma gases. None of these gases could be used pure as plasma gas because of the lack of higher power sources required for the high gas flows necessary to cool the electrodes properly. Diluted strongly with argon, all of the gases, except carbon monoxide, gave stable operating plasma jets. However, the ratios of diluting gas to reactive gas, were very high, see Table III. Carbon monoxide corroded the electrodes owing to decomposition into carbon and oxygen so quickly that, even in large dilution with argon, stable

TABLE III

Gas	Gas Flow l/min.	Argon l/min.	Electrical Characteristics			Operation Time sec.	Corrosion
			V	Amp.	KW		
Ammonia	0.4	17.9	45	150	6.75	15	slight
Carbon monoxide	3.1	5.8	35	350	12.25	60	W-cathode molten
Methane*	0.5	7.0**	43	300	12.9	30	Anode corroded
Hydrogen*	6.5	20.3	28	325	9.15	60	Anode corroded

*   A consumable ordinary graphite cathode was used
** Nitrogen was used as diluting gas

operation was impossible.

2. Preparation of Compounds

a. The preparation of cyanogen:[5]-- The preparation of cyanogen according to the endothermic reaction:

$$2C + N_2 \rightarrow (CN)_2 - 71 \text{ Kcal.}$$

which was mentioned earlier by Stokes and Knipe,[3] was investigated by reacting the carbon vaporized from an ordinary graphite cathode with a nitrogen jet - or an argon jet with nitrogen fed into the "flame" of the jet. Both methods gave the same results - conversions up to 15%, based on the carbon input, even when the electrical characteristics and the carbon-nitrogen ratios were quite different. The unconverted carbon (80%) was collected as very fine soot. No

(5) H. W. Leutner, "The Production of Cyanogen from the Elements Using a Plasma Jet. Graphite and Pyrolitic Graphite Successfully Used as Electrode Materials," Ind. & Eng. Chem., In press (1962).

paracyanogen was present in the soot, as the negative result of the Prussian Blue reaction proved after intensive treatment with concentrated potassium hydroxide solution.

In order to find out if additional quenching affects the results, through the bottom of the tubing a water-cooled copper funnel and other quenching devices were introduced to quench the gases coming out of the jet, see Fig. 10. Surprisingly, the fast quenching had a negative effect on the yields not yet explained, reducing them to one half of the yields obtained without cooling. The reduction might be due to a too short reaction time or to a catalytic decomposition of cyanogen by the copper of the cooling funnel. The reaction time in the plasma flame was calculated to be in the range of 5 to 50 milliseconds, depending on the gas-flow rate. The reaction temperature was not measured, but was certainly substantially higher than 4000°C., since all the carbon was definitely vaporized. Besides cyanogen and soot, only para-cyanogen could be observed qualitatively, especially when relatively large quantities of carbon were consumed. Table IV gives the typical data on the conditions and results of some of the experiments.

TABLE IV

Gas Flows l/min.	Electrical Characteristics			Nitrogen-Carbon Ratios	Carbon Consumed mg/min.	Cyanogen Obtained mg/min.	Conversions based on Carbon Input 2
	V	Amp.	KW				
Nitrogen as plasma gas without cooling							
7.0	46.0	240	11.0	21.9:1	342	91.5	12.25
7.0	44.0	270	11.9	17 :1	440	130.0	13.55
7.0	41.0	300	12.3	13.7:1	492	147.6	13.9
Nitrogen as plasma gas with cooling							
7.0	42.5	235	10.0	15.8:1	474	74.5	7.3
7.0	43.0	280	12.0	12.8:1	542	92.7	7.1
Argon as plasma gas without cooling. Feeding rate for nitrogen: 2.0 liters/min.							
11.9	23.5	410	9.6	3.8:1	566	177	14.45
11.9	24.0	430	10.3	3.6:1	928	276	13.8*
17.9	24.0	400	9.6	2.1:1	1045	342	14.95
Argon as plasma gas with cooling. Feeding rate for nitrogen: 2.0 liters/min.							
17.9	22.8	405	9.25	2.12:1	1007	168	7.7
17.9	24.0	400	9.6	1.4 :1	1509	215	6.7

*Feeding rate for nitrogen: 3.15 liters/min.

Methods of Analysis

The products obtained were analyzed by chemical methods.

The product gases from the cooling chamber were led through a glass tube packed with glass wool to retain the finely divided soot and then passed through a 3"-diameter glass column 3' in length packed with Raschig-rings counter-currently to a flowing 0.5 N. potassium hydroxide solution. (When cyanogen was to be determined separately, a 0.5 N. ammonia solution was used). The dissolved, or hydrolized, compounds in the solution were collected and analyzed. The undissolved gases were collected over water for further analysis. See Fig. 10 for details.

Cyanogen Determination

The cyanogen formed was hydrolized by the potassium hydroxide:

$$2KOH + (CN)_2 \rightarrow KCN + KOCN + H_2O.$$

The analysis of the cyanide formed was easily carried out gravimetrically by precipitation as silver cyanide, or better, by using the Liebig-Denieges method of titrating the potassium cyanide with a 0.1 N. silver nitrate solution.

b. The preparation of hydrocyanic acid:-- Encouraged by the production of acetylene[4] and cyanogen[5] in the plasma jet, the synthesis of another simple endothermic compound, hydrocyanic acid, HCN, was investigated. The formation of HCN was likely,

since the heat of formation from the elements of gaseous hydrocyanic acid is -30.1 Kcal/mole, similar to the heat of formation of acetylene (-54.3 Kcal/mole) and since any cyanogen formed should react at the high temperatures of the plasma jet with hydrogen to form HCN.

Five different reactions were carried out in a plasma jet by using compounds of carbon, hydrogen and nitrogen in different ratios as starting materials, in order to obtain hydrocyanic acid.

b-1. From the Elements

According to the reaction:

$$2C + H_2 + N_2 \rightarrow 2HCN -60.2 \text{ Kcal.}$$
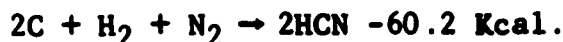
Solid carbon in a hydrogen-gas suspension might be fed into the "flame" of a nitrogen plasma to give, after fast quenching, HCN. In order to avoid energy and time consumption for heating up the carbon particles, the experiments described below were carried out with a consumable ordinary graphite cathode as the carbon source, nitrogen as plasma gas, and hydrogen fed through the gas-feeding ring, Fig. 7, into the "flame" of the plasma jet. In order to maintain unchanging electrical characteristics, the cathode was pushed continuously towards the anode to compensate for the vaporization of the graphite cathode. Table V shows the experimental data and the results obtained in these experiments.

TABLE V

| Starting Ratio | | Power Input | HCN-Formation* | | C_2H_2-Formation* | |
C:N	C:H	KW	%	gr/min.	%	gr/min.
1:9.6	1:7.8	13.3	43.3	1.0	13.9	0.18
1:9.2	1:4.6	12.8	51.1	1.0	12.9	0.12**

* Product formation is based on the carbon input.
** Without using a cooling funnel for fast quenching of the products
formed.

Over 50% conversion into HCN, based on the carbon input, was obtained. The only significant byproduct of the reaction was acetylene. Other hydrocarbons were formed but in yields of less than 2%, based on the carbon input, as the gas analysis of the collected gases showed. The remaining carbon input was collected as finely divided soot in the cooling chamber. A limiting factor of the method described is the relatively small vaporization rate of the graphite cathode (approximately 1 gram/min.). When quenching was not so pronounced, by omitting the water-cooled funnel below the plasma "flame," higher HCN yields were observed.

b-2. From Carbon and Ammonia

The method used differed from the method described under a. only by feeding ammonia through the gas-feeding ring into the "flame" of the nitrogen plasma jet instead of hydrogen and by forcing the vaporization rate of the graphite cathode. The results were similar to those obtained by using hydrogen. Ammonia was

decomposed quantitatively into nitrogen and hydrogen while passing through the plasma "flame"; the hydrogen determinations by gas analysis of the gases obtained were in agreement with the calculated values for complete decomposition of ammonia. Table VI shows the experimental conditions and results.

TABLE VI

Starting Ratio		Power Input	HCN-Formation*		C_2H_2-Formation*	
C:N	C:H	KW	%	gr/min.	%	gr/min.
1:7.8	1:2.8	13.3	33.8	1.0	No values	
1:10	1:6	13.6	37.3	1.0	6.9	0.1
1:9	1:6.7	12.9	39.0	1.0	17.8	0.2**

* Product formation is based on the carbon input.
** Without using a cooling funnel for fast quenching of the products formed.

In accordance with the results obtained under a., the yield increased by omitting the cooling funnel. The higher carbon input did not incrase the yields, as contrarily to expectation; the amount of product formed per time unit remained the same.

b-3. From Methane and Nitrogen. Nitrogen Fixation

The carbon vaporization rate in the preceding experiments was low. By feeding methane into the plasma "flame," decomposition into carbon and hydrogen was expected. This would increase the carbon supply and at the same time provide the hydrogen necessary for the HCN formation.

Both graphite and nonconsumable 2% thoriated tungsten electrodes were used. Into the pure nitrogen plasma "flame," methane was added through a gas-feeding ring. As the gas analysis of the collected gases showed, 92-95% of the methane input was decomposed into the elements. In various cases, after 2 to 3 minutes of reaction, the anode and/or the gas-feeding ring were blocked owing to a heavy soot formation. By using the circular gas feeder, with the 30° angle to the plasma "flame" axis, this difficulty was overcome and large excesses of methane could be used. Table VII, gives the experimental data and the results obtained in these experiments. All of these reactions were carried out without a cooling funnel for fast quenching of the products formed.

As it is shown in Table VII higher HCN yields are obtained by using a large excess of nitrogen. With a pyrolytic graphite cathode and nitrogen in the C:N proportion of 1:7.7 a conversion into HCN and C_2H_2 of 91.3% of the total carbon input was achieved although the amount of products formed is relatively low compared with 1.9 grams per minute of HCN and 1.5 grams per minute C_2H_2, using a stoichiometric C:N ratio, high gas flows and a 2% thoriated tungsten cathode. Other hydrocarbons besides C_2H_2 were not present; cyanogen was found in not quantitatively detectable amounts.

The experiments listed are also important on the view point of nitrogen fixation; in some cases more than 20% of the

TABLE VII

Methane Input l/min.	Starting Ratio C:N	Ratio C:H	Power Input KW	HCN-Formation* %	gr/min.	C_2H_2-Formation* %	gr/min.	Conversion Based on Nitrogen %
a) Using Graphite Cathodes								
2.0	1:4	1:2.5	12.7	31.5	1.5	40.3	0.9	7.17
4.0	1:3.1	1:2.9	12.2	21.1	1.4	39.4	1.3	6.82
2.0	1:7.7	1:3.6	12.5	45.7	1.2	45.6	0.6	5.8**
b) Using 2% Thoriated Tungsten Cathodes								
3.25***	1:1.5	1:3.17	11.5	23.2	1.0	62.3	1.4	21.9
8.0	1:1	1:4	12.5	19.5	1.9	31.75	1.5	20.3

* Product formation is based on the total (cathode and methane) carbon input.
** Pyrolytic graphite was used as cathode material.
*** Circular, 30° angle-gas feeder was used.

nitrogen input was converted into HCN, being C_2H_2 the main product obtained from CH_4 + N_2.

b-4. From Ammonia and Methane

In order to switch from the assembly with consumable graphite electrodes to a nonconsumable cathode, in the following experiments stoichiometric mixtures of ammonia and methane were fed into the "flame" of either an argon plasma jet or a nitrogen plasma jet. Since the previously described experiments showed that CH_4

is almost quantitatively decomposed into its elements in the plasma "flame," methane was chosen as carbon and hydrogen source. Ammonia was used as nitrogen source instead of pure nitrogen, in order to avoid heat losses for breaking up the strong nitrogen molecule into atomic nitrogen; hydrogen was therefore used in large excess (from NH_3 and CH_4). Essentially the same results should be obtained by feeding a nitrogen-methane mixture instead of an ammonia-methane mixture into the plasma "flame "; higher electrical power would be necessary. The experiments listed in Table VIII were all carried out by using the circular gas-feeding device with gas input perpendicular to the "flame" axis.

As Table VIII shows, the conversion to hydrocyanic acid and acetylene based on the carbon (methane) input ranged between 60-75%, using as well argon or nitrogen as plasma gases. By using nitrogen, either as pure nitrogen plasma or added in small amounts to an argon plasma (N_2 in excess), preferably HCN-formation was achieved yielding up to 50% based on the carbon (methane) input. With argon as plasma gas, C_2H_2-formation has the preference, the respective yields being reversed. The preference of HCN-respectively C_2H_2-formation is dependable on the quenching rate. Since acetylene is a more endothermic compound than hydrocyanic acid is, (54.3 Kcal/mole for C_2H_2 compared to -30.1 Kcal/mole for HCN) the faster the quenching the higher the C_2H_2-formation would be.

TABLE VIII

Plasma Gas Flow l/min.	Starting Ratio C:N	C:H	Power Input KW	Stoich. CH_4+NH_3 Input l/min.	HCN-Form. % gr/min.	C_2H_2-Form. % gr/min.	Cooling Funnel	Conversion Based on Nitrogen
a) Argon as Plasma Gas								
14.35	1:1	1:7.25	8.8	4.0	32.2 0.78gr.	42.9 0.45gr.	yes	
15.75	1:1	1:6.7	8.6	6.0	31.9 1.15gr.	30.0 0.52gr.	no	
11.9	1:1	1:7.0	9.9	10.0	30.8 1.86gr.	39.75 1.18gr.	no	
11.9	1:0.97	1:6.8	9.2	10.0	28.55 1.74gr.	44.1 1.3gr.	yes	
11.9	1:0.97	1:6.8	15.6	10.0	25.0 1.67gr.	48.7 1.6gr.	no	
11.9*	1:1.56	1:6.7	11.2	10.0**	36.0 2.2gr.	25.7 0.7gr.	no	
b) Nitrogen as Plasma Gas								
7.0	1:8	1:7.1	15.5	4.0	47.2 1.13gr.	21.6 0.25gr.	yes	6.5%
5.0	1:4.3	1:4.7	14.8	6.0	51.7 1.88gr.	20.7 0.38gr.	no	13.5%
4.15	1:2.6	1:6.8	14.0	10.0	40.0 2.4gr.	32.9 1.0gr.	no	18.4%

* 1.7 l/min. Nitrogen was added to the plasma gas.
** Gas mixture was fed through the circular gas feeding ring with a 30° angle vs. the plasma flame.

The quenching rate obviously varies with the electrical power input, the plasma gas flow used, the feeding rate of the reactive gases and the quenching effect of the cooling devices.

With the reaction conditions and the apparatus described, fast quenching with the cooling funnel introduced 1-1/2" underneath the anode end favored the C_2H_2 formation using argon as plasma gas. When using the same quenching devices, higher power input through the argon plasma jet also favored the formation of acetylene (because of the raising temperature) in accordance with the theory. Highest HCN conversions were obtained in a nitrogen plasma jet with gas flows between 5-7 liters per minute. Lowering the gas flow rates, causing higher plasma jet temperatures, the acetylene formation was again favored. The residence time of the particles in the plasma was calculated to range between 1 and 20 millisec. depending on the gas flow rates.

Besides HCN and C_2H_2, small quantities of cyanogen, $(CN)_2$, were formed; maximum amount of $(CN)_2$ found was 0.8%, based on the carbon input. No paracyanogen was present in the soot (average yield: 20% of the carbon input) as the negative result of the Prussian Blue reaction proved after intensive treatment with concentrated potassium hydroxide solution. The collected gases contained, besides C_2H_2, between 2 and 5% hydrocarbons, based on the carbon input, as was found by gas analysis. It is assumed that unreacted

methane was collected and that no other hydrocarbons were formed.

Here again the high conversion rates, up to 20% based on the nitrogen input, might be pointed out as an interesting method of nitrogen fixation.

b-5. From Ammonia and Carbon Monoxide

An additional possibility for the production of HCN in a plasma jet seems to be the reaction of water gas ($C + H_2O \rightarrow CO + H_2$) with generator gas ($C + Air \rightarrow CO + N_2$) according to

$$N_2 + 3H_2 + 2CO \rightarrow 2 \; HCN + 2 \; H_2O$$
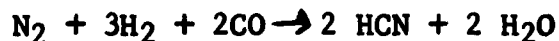
In order to find out if this reaction could be accomplished, stoichiometric mixtures of carbon monoxide and ammonia were fed into the "flame" of an argon plasma jet and into a nitrogen plasma jet.

As was found by gas analysis, only the ammonia was decomposed into its elements in the plasma "flame;" the carbon monoxide remained as molecule, due probably to not high enough temperatures. (Decomposition temperature of CO:). The decomposition of CO would be achieved either by using a plasma jet device which would allow operation with carbon monoxide as plasma gas or by feeding the gas into the hottest part of the plasma "flame," close to the cathode.

Methods of Analysis

The same apparatus as described for the preparation of cyanogen (p. 16) was used to analyse the products formed.

HCN Determination

HCN reacted with the basic solution (KOH or NH_4OH) according to

$$KOH + HCN \rightarrow KCN + H_2O.$$

The cyanide formed was determined by using the Liebig-Denieges method of titrating the potassium cyanide with 0.1 N. silver nitrate solution.

$(CN)_2$ Determination

In the presence of hydrocyanic acid, the cyanogen determination was carried out by using ammonia solution instead of potassium hydroxide in the column. Cyanogen reacts with ammonia to form hydrocyanic acid and urea:

$$(CN)_2 + NH_4OH \rightarrow CO(NH_2)_2 + HCN.$$
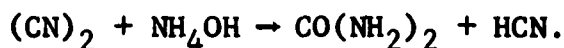
The urea formed was determined gravimetrically after evaporating the solution to dryness on a water bath in a platinum beaker, followed by a drying process of more than 3 hours in a drying oven. Only insignificant amounts of cyanogen, ranging from 0.52 to 0.7% of the total carbon input, were found.

Acetylene Determination

The determination of acetylene was made by gas analysis and by titration with a 0.1 N. $Na_2S_2O_3$ solution of the previously

oxidized copper acetylide obtained by precipitation from a basic copper-I-solution.

Gas Analysis

The gas analysis of the collected gases was carried out in an Orsat apparatus with the commonly used reagents. Hydrogen was determined by passing the gas over CuO at approximately 650°C; the hydrocarbon values were obtained by measuring the CO_2 absorption after combustion. Determination of carbon dioxide, oxygen, acetylene, hydrogen and hydrocarbons formed were made for all the listed experiments. The results were in accordance with the starting materials input and the compounds obtained.

c. The reduction of aluminum oxide:-- The use of the high temperatures of the plasma jet to carry out reductions is certainly an attractive possibility. The investigations described here on the reduction of alumina are to be considered only as preliminary studies. Aluminum oxide is a strongly exothermic compound. It was believed that Al_2O_3 decomposed into the elements, aluminum and oxygen, upon passing through the plasma "flame." Since the heat of formation of Al_2O_3 is very high (+389.5 Kcal/mole), fast quenching was necessary to prevent recombination of the elements to alumina.

Several experiments were made with an argon-plasma jet. Into the "flame" of the jet commercial c... grade Al_2O_3 (200 mesh) was fed as a suspension in either hydrogen or methane by the powder

feeding apparatus (Fig. 9) and through the powder-feeding ring

(Fig. 6). The residence time of the particles in the plasma "flame"

was calculated to range between 5 and 20 millisec. The solid

products formed, after fast quenching with the water-cooled funnel

located 1-1/2" below the anode end, were collected in the copper

collector attached to the cooling funnel.

The results obtained are listed in Table IX.

TABLE IX

Al_2O_3 Input gr/min.	Gas	Carrier- Flow Rate 1/min.	Argon Flow Rate 1/min.	Power Input KW	Conversion Based on Al-Input %	Method of Analysis
6.0	H_2	12.0	15.5	8.55	1.25	gravimetric
1.5	CH_4	8.5	11.9	8.9	0.2	H_2-evolution
3.0	CH_4	8.7	11.9	9.6	0.2	H_2-evolution

The reduction to aluminum metal was very poor in all of the reactions;

although aluminum metal was definitely formed, as was proved by

measuring the hydrogen gas obtained by reaction with acids and by

gravimetric analysis. (The powder collected was treated with half

concentrated hydrochloric acid, precipitated as aluminum hydroxide

and weighed as aluminum oxide).

Since the particle size of the collected reaction product, which consisted essentially of aluminum oxide, was the same as the size of the starting material, it is assumed that either the residence time in the plasma "flame" was too short or the products were not added into a hot enough part of the "flame," thereby limiting the decomposition of the alumina.

d. Other reactions:-- Several test reactions are described which were carried out in order to complete information about earlier experiments.

d-1. Nitrogen-Hydrogen Reaction

Gaseous endothermic compounds were easily obtained at the temperatures of the plasma jet. By feeding hydrogen into the "flame" of a nitrogen plasma, the formation of the exothermic compound, ammonia, was expected:

$$N_2 + 3H_2 \rightarrow 2NH_3 + 11 \text{ Kcal.}$$

The plasma-jet apparatus described under 2. using a 2% thoriated tungsten rod as cathode and the same collecting devices for the products formed, were used. With gas flows of 5.1 l/min. of nitrogen and 8.8 l/min. of hydrogen and a power input of 13.2 KW, no ammonia could be detected by Nessler's reagent in the solution obtained from the column filled with Raschig-rings (distilled water in counter-current). By adding 0.1 N. iodine solution to the collected aqueous solution, appreciable amounts of iodine were needed for neutralization. Probably small amounts of

hydrazine, N_2H_4, (heat of formation: -1.7 Kcal/mole) were formed instead of the expected ammonia.

d-2. Nit ogen-Oxygen Reaction

The formation of oxides of nitrogen in a plasma jet, described earlier,[3] was repeated with the modified equipment described. Into the "flame" of a nitrogen plasma jet, oxygen was fed in the stoichiometric ratio. With a 2% thoriated tungsten rod as cathode, a power input of 15 KW and gas flows of 5.5 l/min. of nitrogen (plasma gas) and oxygen, only 2.03% of the total nitrogen input was converted into NO. This result is in agreement with the results obtained earlier and shows a poor rate for nitrogen fixation compared with the rates reported under 2c.

d-3. The Preparation of Acetylene From the Elements

The formation of acetylene from the elements by using a mixture of hydrogen and argon as plasma gas and by using the anode (graphite) as carbon source was reported earlier.[4] The yield obtained was 33.7% at a C_2H_2 formation rate of 50 mg/min.

Experiments with an argon plasma jet, a consumable graphite electrode as carbon source and hydrogen fed into the plasma "flame" gave higher yields and ten times higher C_2H_2 formation rates per time as shown in Table X.

TABLE X

Argon Flow 1/min.	Hydrogen Flow 1/min.	Carbon Input gr/min.	Power Input KW	C_2H_2-Conversion %	Amount Produced gr/min.
23.2	6.5	1.05	8.8	42.2	0.5
16.1	6.85	0.86	9.0	39.2	0.35

B. The Radiofrequency Plasma Jet

1. The Preparation of the Oxides of Nitrogen

The preparation of the oxides of nitrogen under reduced pressure was investigated with the 300-watt unit. The tank-coil tube was enclosed in a water-cooled glass tube which was attached to 2 glass traps, one cooled with dry ice-acetone and the other with liquid nitrogen (see Figs. 7 and 8). The entire system was attached to a vacuum pump with an appropriate manometer and valve.

The plasma jet was started by introducing helium at a pressure of about 1/2 atm. and then changing to a nitrogen-oxygen mixture or air. The results of three experimental runs are tabulated in Table XI. As can be seen from the table, the conversions are low. However, the power level of operation is also low and higher conversions can be expected from higher power inputs. The material collected in the liquid nitrogen was blue in color and yielded a red-brown gas upon evaporation. I.R. spectra and a molecular weight determination showed this product to be a mixture of NO and NO_2. A mixture of 50% NO_2- 40% N_2O_4- 10% NO_2 (room temperature

TABLE XI

Run	1	2	3
Gas used	$1:2;N_2:O_2$	$1:1;N_2:O_2$	Air
Total gas flow (cc/sec.)	6	5	6
Total power to jet (watts)	375	394	375
Running time (hours)	4.5	1	2.5
System pressure (mm Hg.Abs.)	117.5	75	110
Amount of Material Collected dry ice trap (cc)	nil	nil	nil
liquid nitrogen trap (cc)	0.5	0.2	0.4
% Conversion (based on conversion to NO_2)	1	1½	2
Average molecular wt. of product	58	51.2	56
Identification by I.R. spectra	NO, NO_2	--	NO, NO_2

equilibrium) has a molecular weight of 56.6 which is in close

agreement with the experimental values. A sample of the product

was allowed to react with oxygen and the I.R. spectrum showed

the reaction product to be entirely NO_2. Mixture ratio of N_2 to O_2

seemed to have no effect on the type of oxide of nitrogen found

(in all cases NO and NO_2).

III. DISCUSSION OF RESULTS

The production of compounds with the plasma jet depends on the temperature achieved and the quenching velocity of the compounds formed at these temperatures. The process of the formation of compounds by using a plasma jet as the high-temperature source may be considered as occurring in two principal steps. Primarily, the decomposition of the molecules, either of the reactive plasma gas or the molecules fed into the plasma "flame," into atoms or activated atoms; and secondarily, the freezing out of the chemical equilibrium attained at these high plasma temperatures by using fast quenching methods.

According to the two steps described above, two essentially different types of chemical reactions might be carried out successfully by the use of the plasma jet temperatures:

First, the decomposition of compounds into their elements or less energetic compounds, e.g. $2NH_3 \rightarrow N_2 + 3H_2$, $CH_4 \rightarrow C + 2H_2$ or $Al_2O_3 \rightarrow 2Al + 3/2\ O_2$.

And second, the formation of endothermic compounds by freezing the chemical equilibria obtained at high temperatures by the use of fast quenching methods. The formation of exothermic compounds, such as ammonia from nitrogen with hydrogen, is impossible, since the chemical equilibrium at high temperatures is less favorable for ammonia than for the elements, nitrogen and hydrogen.

The reactions investigated so far show that by the use of the high plasma jet temperatures with appropriate quenching, gaseous endothermic compounds, such as NO, C_2H_2, HCN and $(CN)_2$ are obtained in as good or better yields than by the best available industrial processes. The formation of gaseous exothermic compounds was not accomplished.

For industrial application of the processes described, it is interesting to point out that electrical current is almost the only cost factor for the compounds obtained since the plant installation equipment and also the raw materials used are relatively cheap. Cost calculations with this small scale plasma jet unit (based only on the power (electricity) input) using the data obtained from the experiments described, give prices which are only double the market prices for acetylene and hydrocyanic acid and even cheaper for the small-scale production of cyanogen. Also, another advantage of plasma-jet processes is the small formation of by-products which make costly separations unnecessary.

An interesting point of view is the high rate of nitrogen fixation by using a nitrogen plasma jet. In some cases, the conversion of nitrogen molecules into nitrogen compounds (HCN) exceeds 20%, thereby doubling the best usual nitrogen-fixation percentages (NO, NH_3, etc.).

CATHODE

ANODE

50 V.

100 V.

750 A.

SHUNT

0-80 V.
0-750 A.

−

+

AIRCO BUMBLEBEE 600 WELDER

TO TRANSFORMER,
RECTIFIERS

REMOTE
SWITCH

240 V.
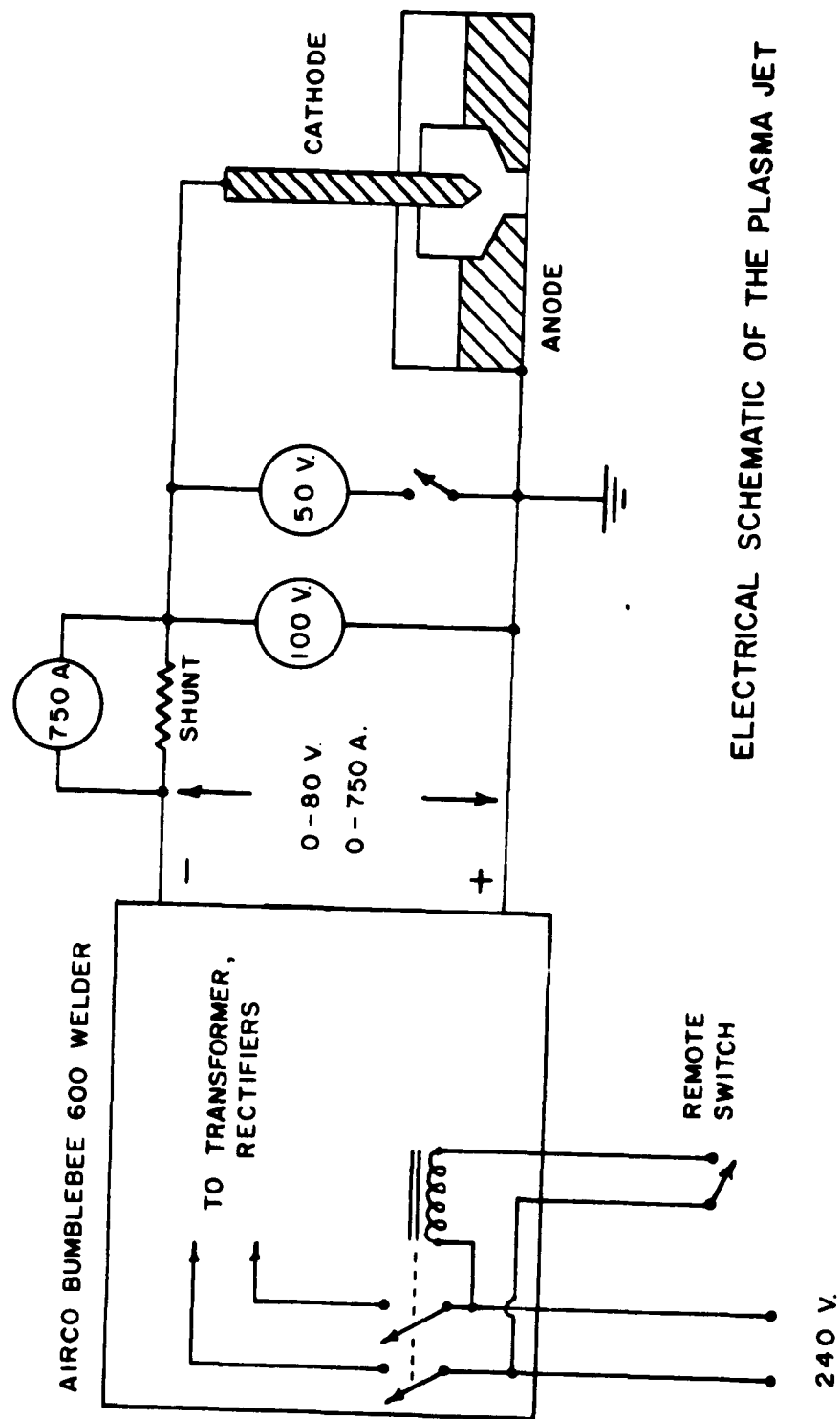
ELECTRICAL SCHEMATIC OF THE PLASMA JET

FIGURE 1.

1. CATHODE ASSEMBLY
2. CATHODE TOP PLATE
3. GAS DISTRIBUTOR PLATE
4. CATHODE BUS BAR
5. CATHODE BUS BAR STUD
6. GAS ENTRY EXTENSION NIPPLE
7. GAS TUBE
8. ANODE ASSEMBLY
9. ANODE ASSEMBLY COVER
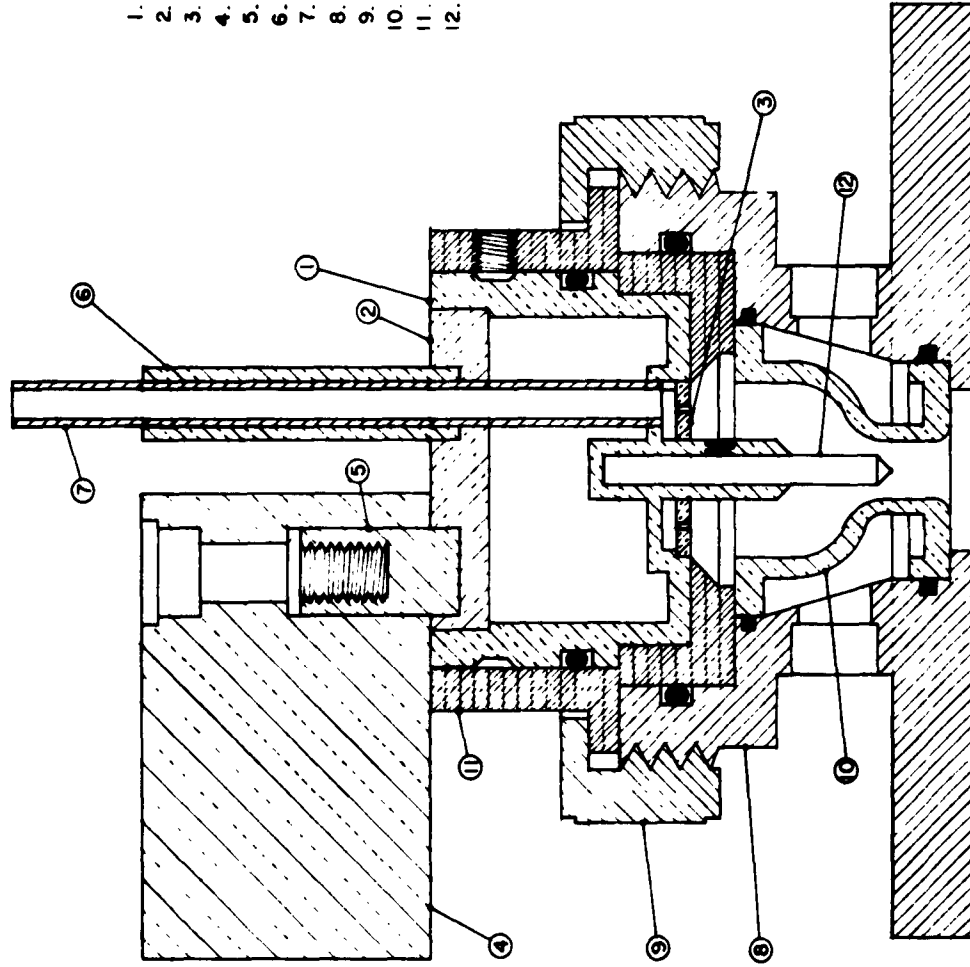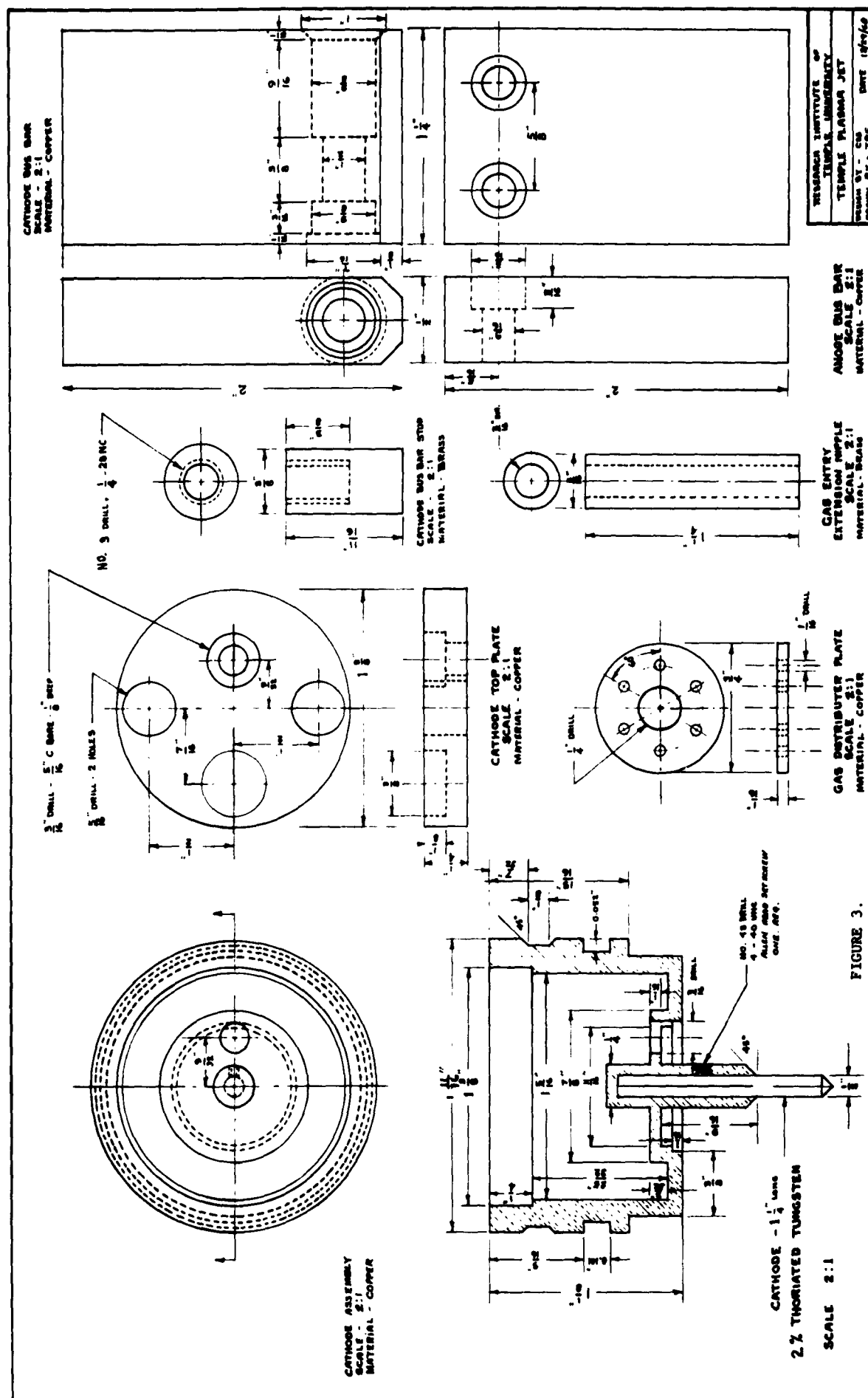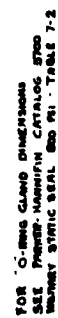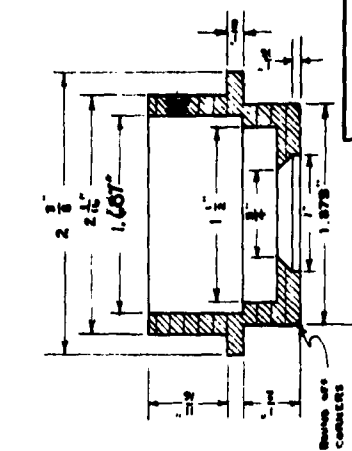10. COPPER ANODE NOZZLE
11. NYLON INSULATOR
12. CATHODE

FIGURE 2.

FIGURE 3.

FIGURE 4.

INSULATOR
MATERIAL - NYLON
SCALE - 1:1

ANODE NOZZLE
MATERIAL - COPPER
SCALE - 2:1

ANODE ASSEMBLY
MATERIAL - 303 S.S.
SCALE - 1:1

COVER
NO TOP VIEW

FOR O-RING GLAND DIMENSIONS
SEE PARKER HANNIFIN CATALOG 5700
SQUEEZE STATIC SEAL 80 PSI TABLE 7-2

(−)
CATHODE

ANODE GRAPHITE INSERT

GAS IN (CH$_4$)

(+)
ANODE

WATER COOLING

FIGURE 5.

O-RINGS

3/8" COPPER TUBE

O-RINGS

3/8" COPPER TUBE

$\frac{7}{16}$

4

$2\frac{7}{16}$

$2\frac{7}{32}$

GAS
INLET

1/8" TUBE

4 - 1/4" MOUNTING
HOLES

O-RING
GROOVE

WATER
IN

WATER
OUT
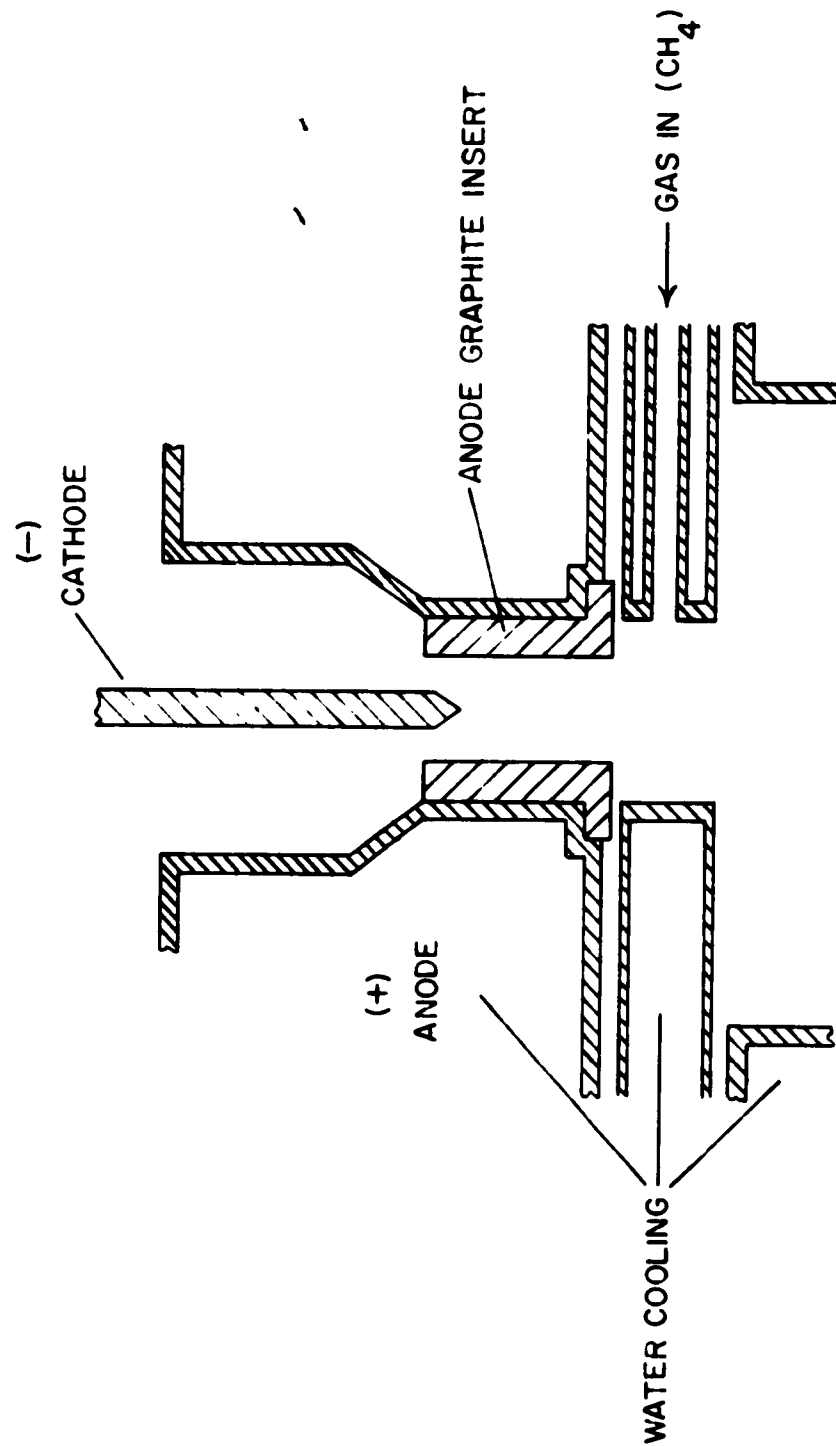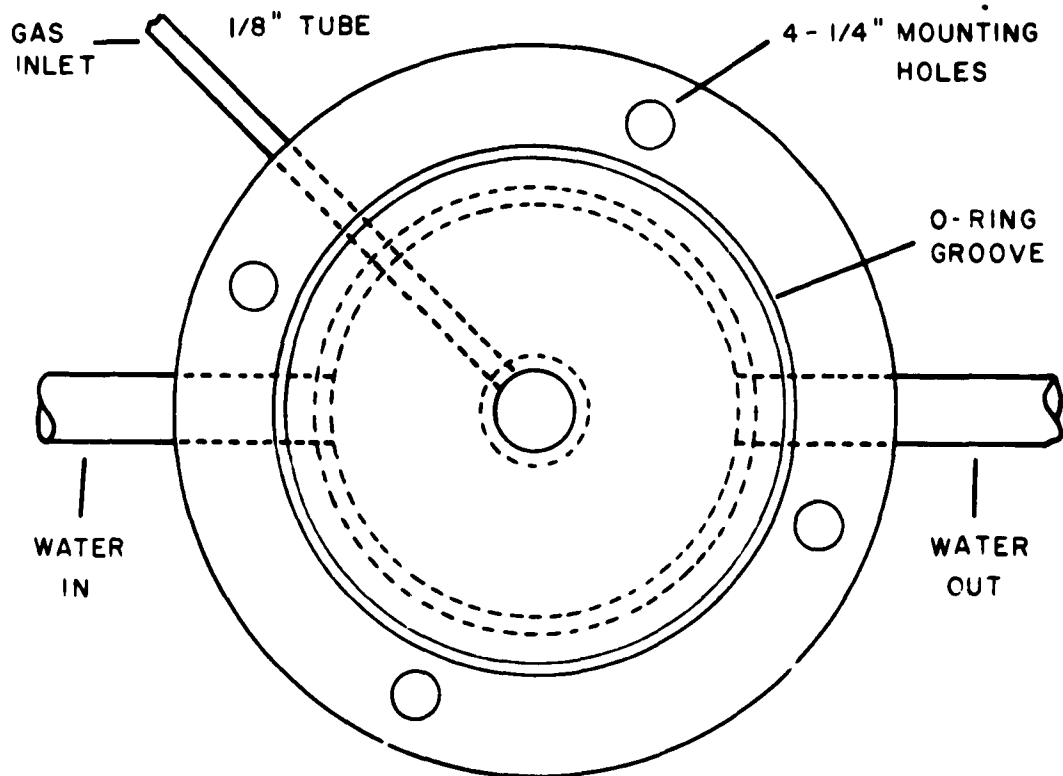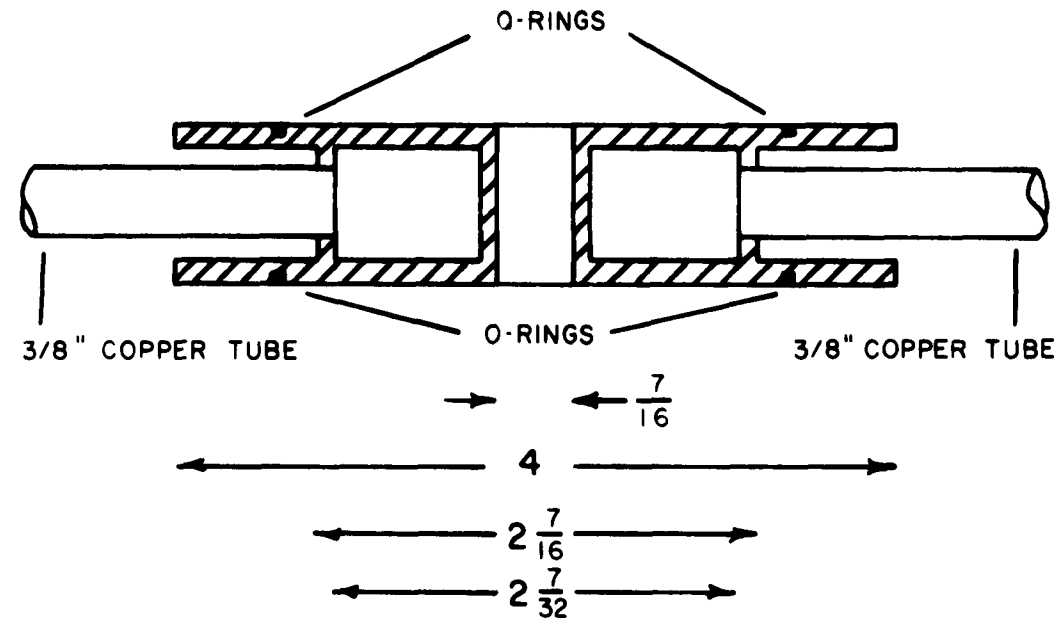
SINGLE ORIFICE FEEDER

FIGURE 6

INSERTS: SCALE: 2:1

8-1/8" HOLES

TYPE A

16-1/32" HOLES

TYPE B

FIGURE 8.

SCALE 1:1

RECESSED HOLES FOR
ALLEN HEAD SCREWS

4 HOLES 1/4"-20 TAP
1/2" DEEP

MATERIAL: STAINLESS STEEL

3/8" FEED TUBE

SOLDERED

22.25°
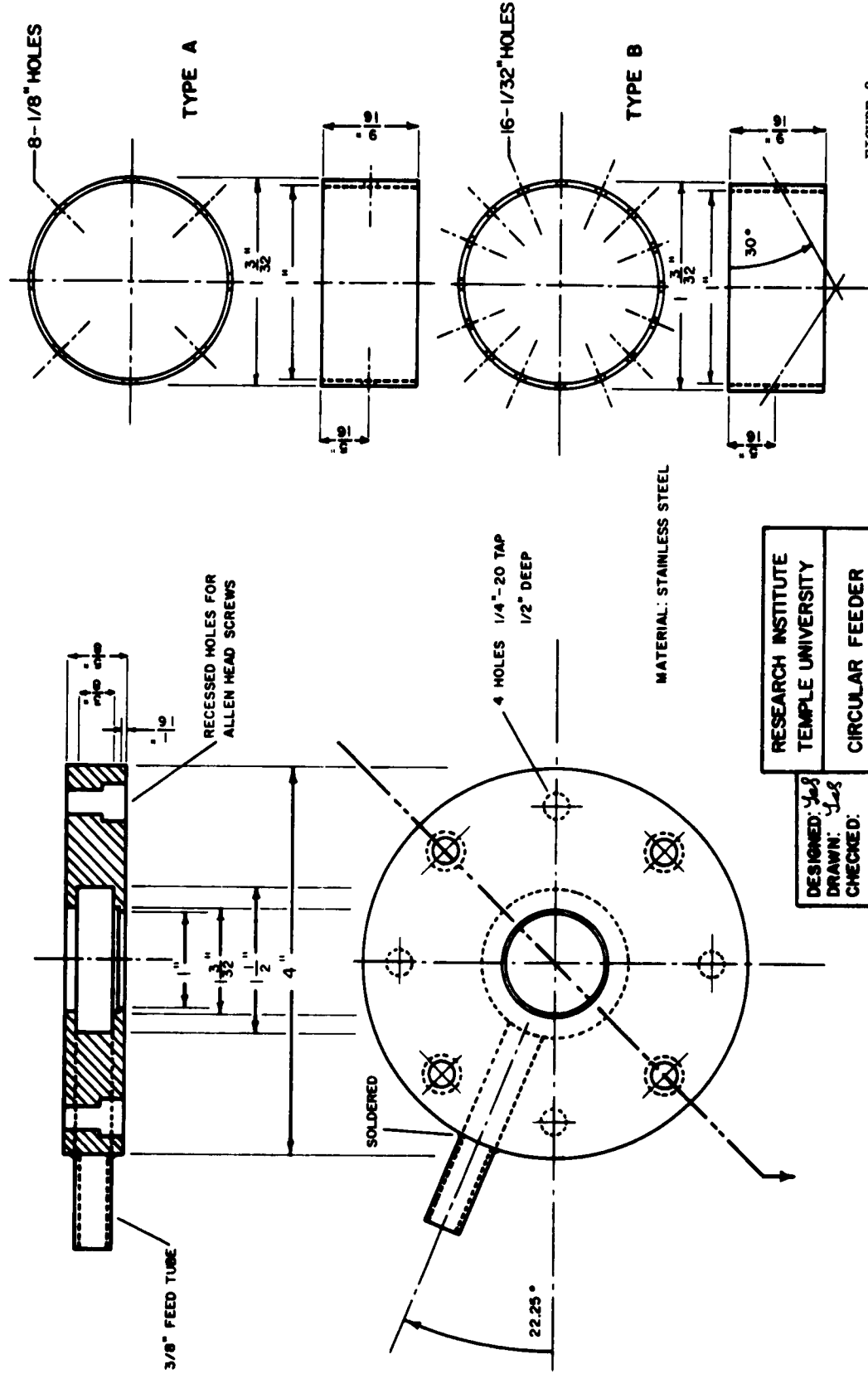
RESEARCH INSTITUTE
TEMPLE UNIVERSITY

CIRCULAR FEEDER

DESIGNED:
DRAWN:
CHECKED:

2-16-62

FIGURE 7.

OVER PRESSURE
LINES

POWDER CHAMBER

O-RING SEALS

1/2" BALL VALVE

MATERIAL:
STAINLESS STEEL

CARRIER GAS

1/4" - 45° FLARE
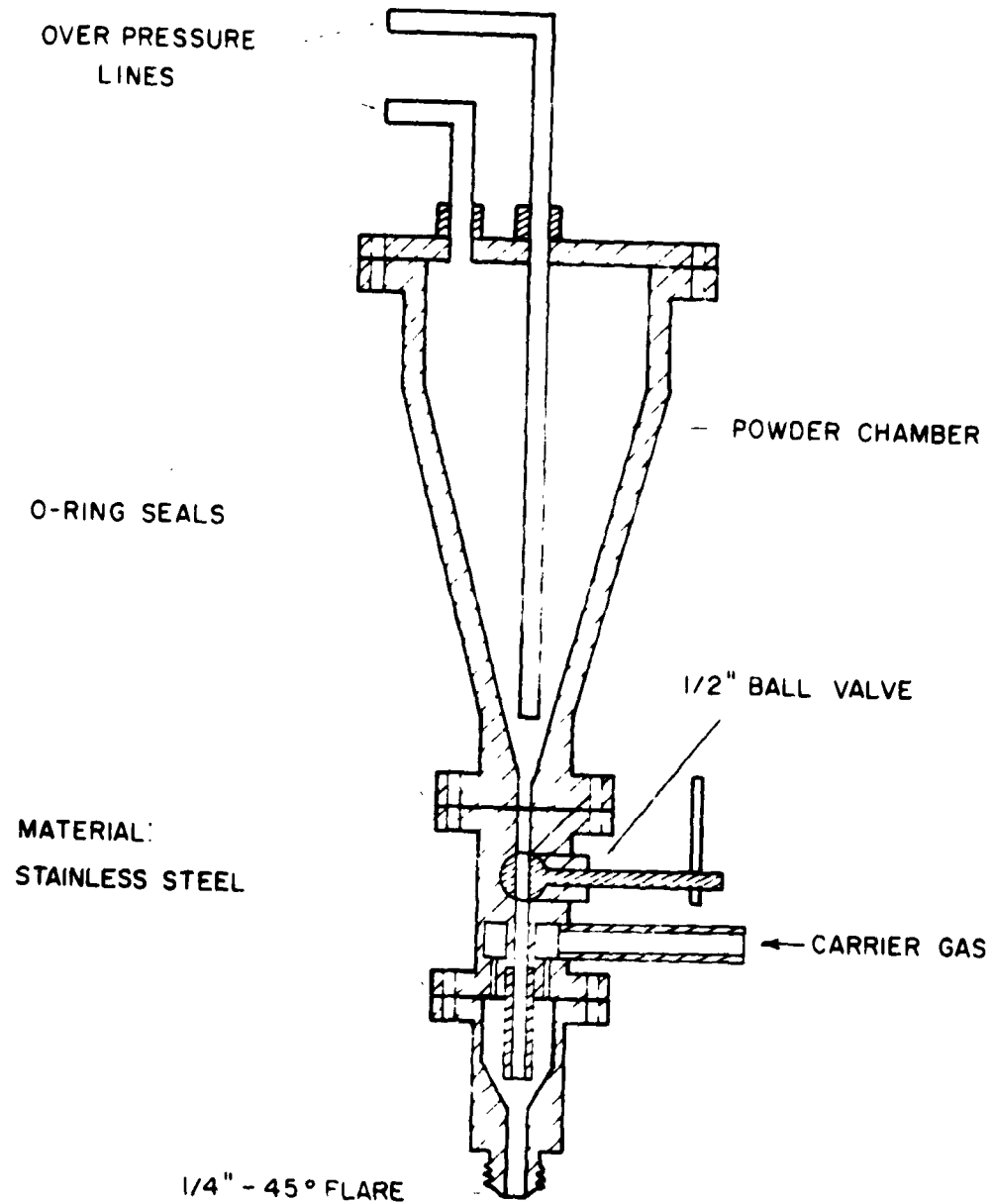
FIGURE 9 - POWDER FEEDING APPARATUS

FIGURE 10

CATHODE

ANODE

GAS IN

WATER COOLED

WINDOWS

QUENCHING CHAMBER

BASE

TO HOOD

GASOMETER

WATER

RASCHIG RINGS

LIQUID COLLECTOR

GLASS WOOL

IN WATER OUT

FEEDBACK LOOP

TANK COIL

450 TH

NC

500

.01   .01

600 MA

RFC

.005

100

RFC   .005

100 MA

3.5 K

7 HY

20   20

6X5   6X5

4 K   .01

VARIAC

5KV

3KV

866

8 HY

4

250 VAC

TO 220 V. FUSE BOX

PLATE

FIL.

PLASMA
CHAMBER

MOLYBDENUM TIP

GAS →

3/8"
COPPER TUBE

OUTPUT
TANK
COIL

4 3/4 TURNS

RUBBER
STOPPER

3/16"
COPPER TUBE

LUCITE
SUPPORT
ASSEMBLY

FIGURE 12.

FIGURE 13.

Research Institute
Temple University
R.F. Plasma Generator

Designed: J.L.S
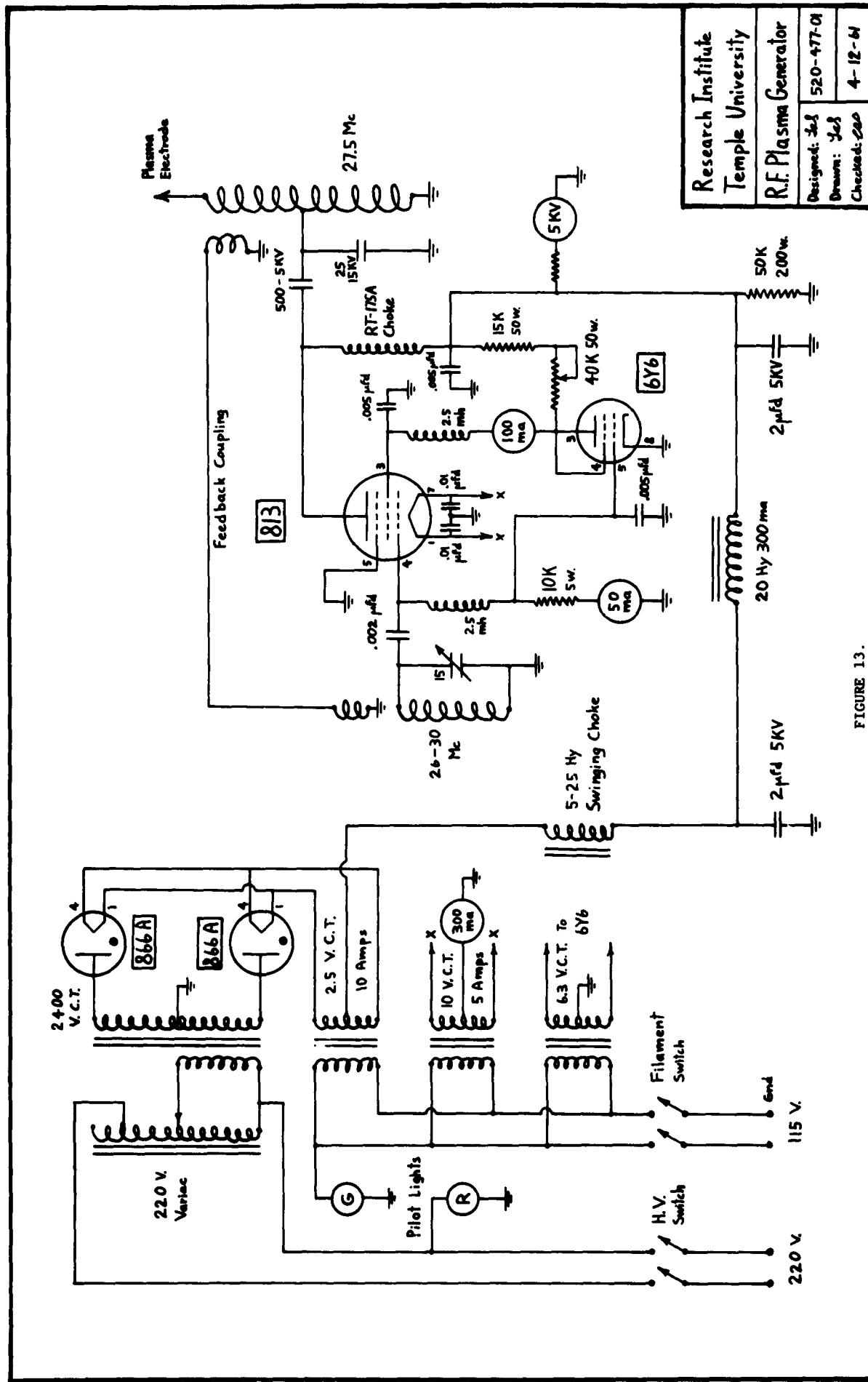Drawn: J.L.S
Checked: D.W.D

520-477-01
4-12-61
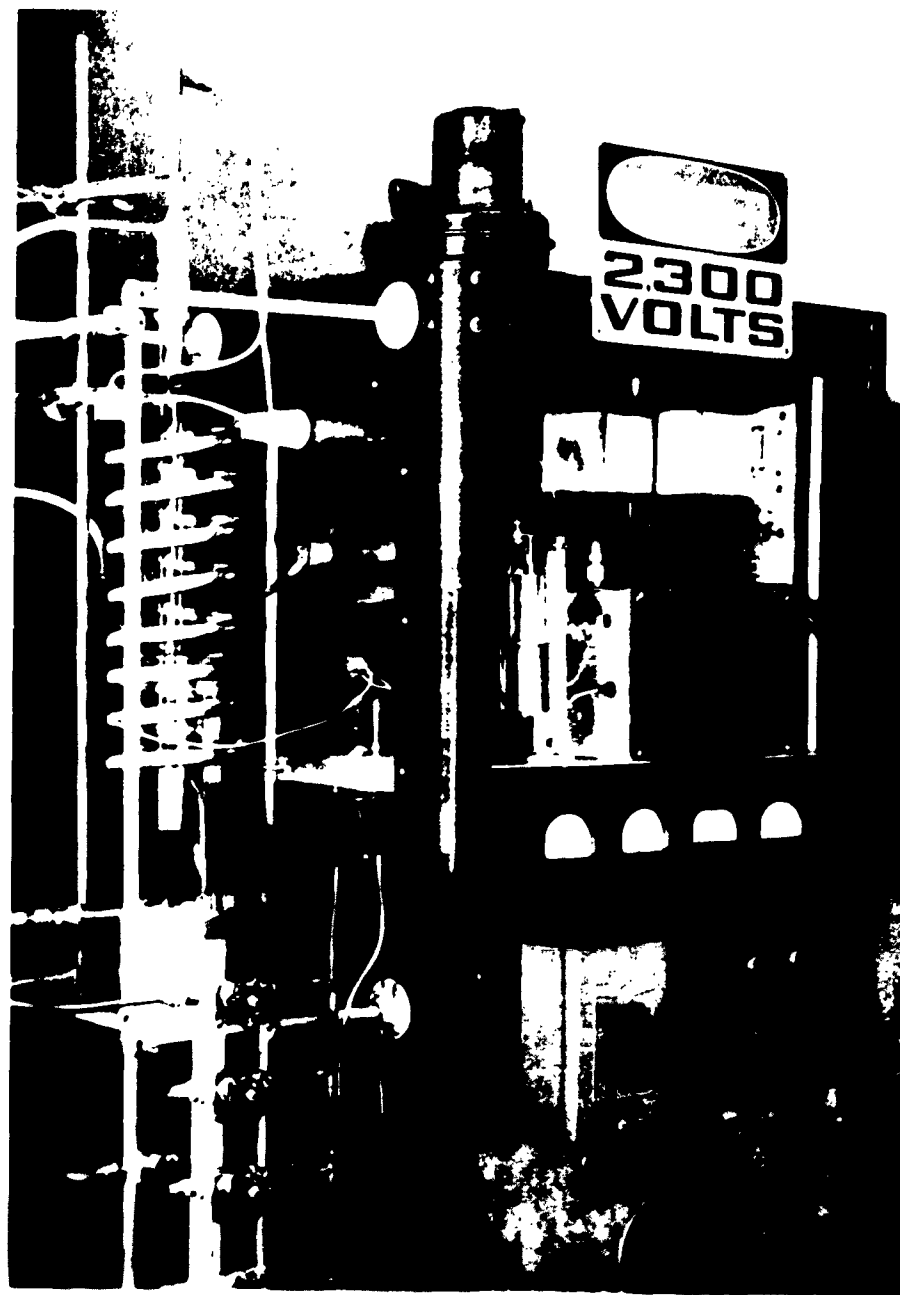
2.300 VOLTS

FIGURE 14.